Electronic Properties of Group V Substituted Fullerene: DFT Approach

Mohamed M. El-Okr, Abd el baset H. Makky, Hanan Elhaes and Medhat A. Ibrahim

Abstract— C59-X (X= C, N, P, As and Sb) was studied by Density Functional Theory DFT at the B3LYP/3-21G** level. Group V elements have been selected to be substituted in the fullerene-C60 cage in order to show the effect of such substations upon structural and electronic properties of the studied molecules. It is found that elements of Group V doped C60 have an electronic structure similar to those of n-type semiconductor. The electronic structure of electron donor (Group V-doped) of the C60 molecules demonstrates the possibility of using these systems in electronic applications as many properties as HOMO–LUMO gaps can be controlled by the appropriate substitution. At the same level of theory the effect of water, methanol, heptanes and acetonitrile upon C60, was studied in terms of geometry, HOMO/LUMO energy and total dipole moment. No changes in the calculated parameters were regarded as a result of solvents.

Index Terms— Molecular modeling; DFT; Electronic properties; Fullerene and Group V elements.

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1 INTRODUCTION

Since the discovery of fullerene molecules C60, in 1985[1-2], considerable effort has been devoted to understanding the properties of this new molecule. Doped fullerenes have also attracted a great deal of interest due to their remarkable structural, electronic, optical, and magnetic properties [3-4]. The unique structural and electronic properties of fullerenes led to another type of doping, named substitutional doping [3-4], where one or more carbon atoms of fullerene are substituted by other atoms, as well as the endohedral doping and exohedral doping. Molecular nanoscale electronic devices have attracted a great deal of attention in recent years [5]. Carbon fullerene is one of the most stable and a well known nano-scale molecular structure; C60 often acts as a semiconductor. Density functional theory, (DFT) [6] arises from two theorems, the proofs of which were given by Hohenberg and Kohn [7].The use of computational methods, such as Density Functional Theory, to calculate structures of large numbers of molecules is well established [8]. There have been a number of theoretical studies for electronic as well as physical properties of C60. These studies were carried out by semi–empirical methods [9], [11], as well as by ab initio and DFT calculations [12], [14]. Recently C60 continue to be the hottest research topic according to its emerging applications.

C60 was used for the growth of diamond by applying spark plasma sintering [15]. It is used efficiently for photo addition of the amino acid glycine as glycine methyl-ester to produce fulleropyrrolidine for many biological applications [16]. It is

also useful tool for fabrication of efficiently stable bulk hetero-junction solar cells [17].

Also it plays an important role as controlling the performance of polymer solar cells [18]. Finite element method (FEM) was used for vibrational and dynamic analysis of C60 and C30 [19].

Based upon above considerations DFT method at the B3LYP/3-21G* level was used to study C59X where X=C, N, P, As and Sb respectively. Geometry parameters, energy gap and total dipole moment were calculated at the same level of theory. The effect of solvents (water, methanol, heptanes and acetonitrile) upon C60 was studied in terms of total dipole moment and energy gap.
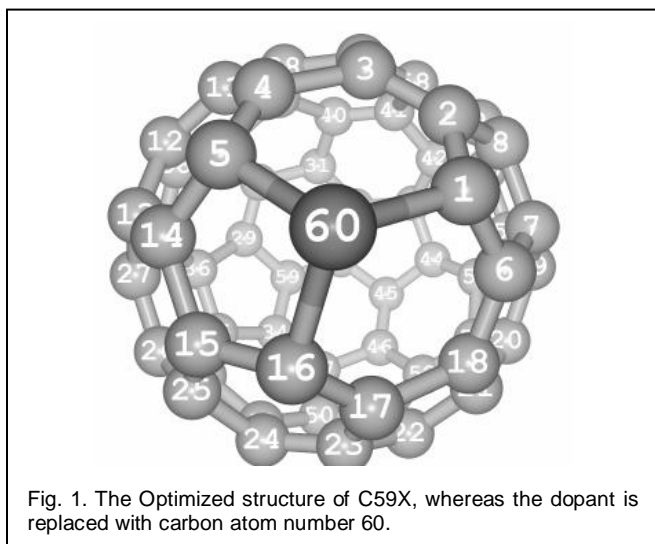
2 COMPUTATIONAL DETAILS

The C60 cage was adopted to provide an initial geometry to generate the heterofullerenes with only one carbon atom displaced by some elements from V Group. Accordingly a model of C59X was constructed as seen in figure 1 whereas X is substituted with C, N, P, As, and Sb respectively. All geometries were fully optimized using the Gaussian 98 suite of programs on a personal computer [20]. Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) [21], [23] was utilized with the 3-21G** basis set to optimize the studied structures. Solvent effects upon C60 were calculated at same level of theory by performing calculations on the optimized structures using the CPCM (conducting polarized continuum model) [24], [25] method. The studied solvents are water, methanol, heptanes and acetonitrile respectively.

3 RESULTS AND DISCUSSION

Fig. 1 presents the optimized geometry of C59X structure. The structure indicate that the X-atom (no 60) is substituted with C, N, P, As, and Sb respectively.

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Fig. 1. The Optimized structure of C59X, whereas the dopant is replaced with carbon atom number 60.

These substituents have selected in order to show the effect of doping on the structural and electronic properties of the fullerene molecules. The optimized bond lengths and bond angles for C60, C59N, C59P, C59As and C59Sb are listed in table 1, which obtained from DFT level calculations at B3LYP / 3-21g**. As indicated in the table 1 fullerene molecule has two different equilibrium bond lengths and two kinds of bond angles [26], [27].

TABLE 1

CALCULATED BOND LENGTHS AND BOND ANGLES AT

DFT-B3LYP/3-21G** LEVEL FOR C60 AND

SPECIFIC FULLERENE DERIVATIVES.

Molecules	C_{60}	C_{59}-N	C_{59}-P	C_{59}-As	C_{59}-Sb
Bond lengths (Å)					
C--C (min)[a]	1.385	1.383	1.382	1.38	1.383
C--C (max)[b]	1.464	1.468	1.495	1.501	1.513
C--X (min)[c]	-------	1.359	1.796	1.935	2.131
C--X (max)[d]	-------	1.434	1.823	1.959	2.161
Bond angles (°)					
C-C-C(min)[e]	108	107.3	107	106.7	106.3
C-C-C(max)[f]	120	121.5	123.5	124.2	125.2
C-X-C(min)[g]	-------	107.6	88.5	83.3	121.1
C-X-C(max)[h]	-------	121.4	123	122.9	123.1

Note: In the Table X(dopant)= N, P ,As, and Sb

a) Minimal value of bond lengths between carbon atoms

b) Maximal value of bond lengths between carbon atoms

c) Minimal value of bond lengths between a dopant and its nearest-neighbor carbon atoms

d) Maximal value of bond lengths between a dopant and its nearest-neighbor carbon atoms

e) Minimal value of bond angles between carbon atoms

f) Maximal value of bond angles between carbon atoms

g) Minimal value of bond angles between a dopant and its nearest-neighbor carbon atoms

h) Maximal value of bond angles between a dopant and its nearest-neighbor carbon atoms

The minimal and maximal values of bond lengths are 1.385 Å and 1.464 Å respectively in case of C60. While the bond angle found to be 108°(the angle between two adjacent single C—C bonds) and 120° (the angle between a double C=C bond and an adjacent single C—C bond).

The optimized geometries for C59N, C59P, C59As and C59Sb clusters still keep the cage structures, but the regular pentagonal and hexagonal rings in C60 are now distorted in C59N, C59P, C59As and C59Sb. The various calculated C---X bonds are in the range of 1.359–2.161Å. The bond lengths increased significantly on going from N toward Sb. As shown in figure 1, it can be expected, bond lengths increase down the group. This means that the stability for the group is decreased by substitution with heavier elements.

Another indication for the geometrical changes according to substations is indicated in terms the surrounding substituted element. The substituted atoms (carbon atoms no 60) is surrounded with three carbon atoms make three bond lengths. The effect of substitutions will be discussed in terms of these three bond lengths. As shown in the table 2, the structure of fullerene, D60 - C1, D60 – C5 and D60 – C16 stand for three groups of non-equivalent carbon sites, there are two types of bond lengths (one pentagons and two hexagons), respectively. The bond lengths (D60 - C1, D60 – C5 and D60 – C16) have been selected to show the effect of substitutions upon the structure of C60. As indicated in the tables, the molecular point group is not changed and remains corresponding to "C1 "point group. Furthermore, except C59-N, all the studied structures have shown an enlargement in their bond lengths as compared with that of C60.

TABLE 2

CALCULATED BOND DISTANCE IN ANGSTROM AND MOLECULAR POINT GROUP FOR C60 AS WELL AS DOPED C60, WHICH CALCULATED AT B3LYP/3-21G**.

Bond distance, Å	C_{60}	C_{59}-N	C_{59}-P	C_{59}-As	C_{59}-Sb
$D_{60} - C_1$	1.385	1.359	1.796	1.935	2.131
$D_{60} - C_5$	1.464	1.434	1.823	1.959	2.161
$D_{60} - C_{16}$	1.464	1.434	1.823	1.959	2.161
Molecular point group	C_1	C_1	C_1	C_1	C_1

Note: In the Table D = C, B, Al, Ga and In respectively.

The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy separation serves as a simple measure of chemical stability [28-29]. This difference is known as the energy gap. Table 3 depicts the character of the HOMO/LUMO energy as (eV) at B3LYP/3-21G** level of C60 and specific fullerene derivatives.

Substitution of "dopant X" = N, P, As, and Sb, atoms on the fullerene C60 (C59X) affects the HOMO and LUMO energies. The calculated (HOMO–LUMO) energy gap of all these C59X clusters are reduced compared with the energy gap of C60. This means that in any excitation process C59-N, C59-P, C59-

As and C59-Sb molecules need more (ca. 1.14, 0.74, 0.69 and 0.086 eV, respectively) energy than that C60.

TABLE 3
CALCULATED HOMO/LUMO ENERGY AS (EV) AT DFT-B3LYP/3-21G** LEVEL FOR C60 AND SPECIFIC FULLERENE DERIVATIVES.

Molecules	C60	C59-N	C59-P	C59-As	C59-Sb
Energy gap	2.89	1.14	0.74	0.69	0.086

This means that in any excitation process C59-N, C59-P, C59-As and C59-Sb molecules need more (ca. 1.14, 0.74, 0.69 and 0.086 eV, respectively) energy than that C60. It suggests that electrons in all C59X clusters are easier to excite from the HOMO to the LUMO than in the case of C60. One might expect to have broad range of new semiconductors because various gaps are formed with respect to the substituents and the range of substitution.

Table 4 shows the calculated total dipole moment for C59X. The calculated total dipole moment was 1.2932, 0.7235, 1.3686 and 2.7509 debye for C59-N, C59-P, C59-As and C59-Sb respectively. One can see from the table that the total dipole moment value of C59-N, C59-P, C59-As and C59-Sb is higher than that of C60.

TABLE 4
CALCULATED DIPOLE MOMENT AS DEBYE AT DFT-B3LYP/3-21G** LEVEL FOR C60 AND SPECIFIC FULLERENE DERIVATIVES.

Dipole moment Contribution as debye	C_{60}	C_{59}-N	C_{59}-P	C_{59}-As	C_{59}-Sb
X	0.0000	-0.0788	-0.7195	1.3683	-2.7507
Y	0.0000	-0.0811	-0.0757	-0.0305	0.0298
Z	0.0000	-1.2882	0.0000	0.0000	0.0000
Total dipole moment	0.0001	1.2932	0.7235	1.3686	2.7509

C60 was subjected to different solvents namely water, methanol, heptanes and acetonitrile upon C60, was studied in terms geometry, HOMO/LUMO energy and total dipole moment. Table5. presents the calculated bond lengths (Å) and bond angles (°) for C60, which described through the polarizable continuum model (CPCM) and calculated by B3LYP methods with 3-21G** basis set. Results indicated that no change is regarded as a result of solvents. At the same level of theory the HOMO/LUMO energy gap as (eV) are calculated in listed in table 6. The studied solvents show no effect and the energy gap remains the same.

TABLE 5
CALCULATED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR C60, WHICH DESCRIBED THROUGH THE POLARIZABLE CONTINUUM MODEL (CPCM) AND CALCULATED BY B3LYP METHODS WITH 3-21G** BASIS SET.

Solvent	Geometry Optimization				Reference			
	CC[a]	CC[b]	CCC[c]	CCC[d]	CC[a]	CC[b]	CCC[c]	CCC[d]
Gas Phase	1.385	1.464	108	120	1.39[e]	1.46[e]	108[f, g]	120[f, g]
Water	1.389	1.461	108	120				
Methanol	1.393	1.457	107.9	120.2				
Heptane	1.389	1.461	108	120				
Acetonitrile	1.389	1.461	108	120				

a) Minimal value of bond length between carbon atoms;
b) Maximal value of bond length between carbon atoms
c) Minimal value of bond angle between carbon atoms;
d) Maximal value of bond angle between carbon atoms
e) David et al., 1991;
f) Yee et al., 2003
g) Tomekia et al., 2005

TABLE 6
CALCULATED HOMO/LUMO ENERGY GAP AS (EV) FOR C60, WHICH DESCRIBED THROUGH THE POLARIZABLE CONTINUUM MODEL (CPCM) AND CALCULATED BY B3LYP METHODS WITH 3-21G** BASIS SET.

Solvent	Energy Gap (eV)	Reference (Ying et al., 1998)
Gas phase	3.01	2.2553
Water	3.007970264	
Methanol	3.007970264	
Heptane	3.007970264	
Acetonitrile	3.007970264	

Finally Table 7 presents the calculated dipole moment as well as its distributions in X, Y and Z directions. C60 shows 0.0 dipole moment this values remain the same and indicates that solvents are not affecting the dipole moment of the C60. A slight change is noticed only for the case of methanol 0.0006 debye.

TABLE 7
CALCULATED DIPOLE MOMENT AS DEBYE AT DFT-B3LYP/3-21G** LEVEL FOR C60 AND SPECIFIC FULLERENE DERIVATIVES.

Dipole moment Contribution (debye)	Gas phase	Water	Methanol	Heptane	Acetonitrile
X	0.0000	0.0000	-0.0002	0.0000	0.0000
Y	0.0000	0.0000	0.0004	0.0000	0.0000
Z	0.0000	0.0000	-0.0004	0.0000	0.0000
Total dipole moment	0.0000	0.0000	0.0006	0.0000	0.0000

4 CONCLUSION

In this work we have studied the structural and electronic properties of C60 and some of its doped derivatives with some elements of group V by performing the Density Functional methods at B3LYP/3-21G** level. Calculated results of C59-N, C59-P, C59-As and C59-Sb molecules are compared with those of C60 at the same level of theory. It is found that these doped derivatives of fullerene have some remarkable features, which are different from and can compete with C60. For the various calculated C---X bonds, the bond lengths for the heaver atoms increased significantly. This means that, the stability of group V is decreased by substitution with heavier elements. There are no changes in the symmetry of the doped fullerenes, while the bond lengths are changed. Dipole moments of the doped C60 with some elements of group V are increased. The HOMO-LUMO energy gaps indicate that these are indeed new family semiconducting systems in terms of various gaps. In summaries, the stability for the group is decreased by substitution with heavier elements. There exists a possibility to produce the semiconductor components of C60-X with various band gaps. Finally solvents show no change in the geometrical, band gap and dipole moment values.

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